

**Final Report to the  
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Thermocapillary-Induced Phase Separation with Coalescence**

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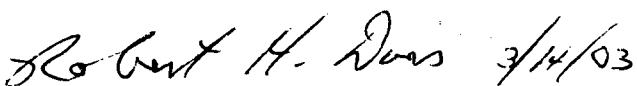
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National Aeronautics and Space Administration  
**THERMOCAPILLARY-INDUCED PHASE SEPARATION WITH  
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## SUMMARY

Research has been undertaken on interactions of two or more deformable drops (or bubbles) in a viscous fluid and subject to a temperature, gravitational, or flow field. An asymptotic theory for nearly spherical drops shows that small deformations reduce the coalescence and phase separation rates. Boundary-integral simulations for large deformations show that bubbles experience alignment and enhanced coalescence, whereas more viscous drops may break as a result of hydrodynamic interactions. Experiments for buoyancy motion confirm these observations. Simulations of the sedimentation of many drops show clustering phenomena due to deformations, which lead to enhanced phase separation rates, and simulations of sheared emulsions show that deformations cause a reduction in the effective viscosity.

## INTRODUCTION

Thermocapillary motion of drops and bubbles in a temperature gradient often leads to undesirable coalescence and phase separation, both on earth and in low-gravity environments. If properly understood, however, thermocapillary effects may be used in a positive way to control multiphase fluid transport and phase separation. Unfortunately, current understanding is primarily limited to the motion of single drops and bubbles, or at most two interacting drops and bubbles, which are often assumed to remain spherical. An outstanding need is for new scientific approaches for the study of the motion of drops and bubbles in concentrated dispersions which exhibit significant distortions of drop and bubble shapes from spherical.

## RESEARCH TASKS

We have sought to meet the outstanding need by employing asymptotic and boundary-integral methods to predict drop interactions and deformations in temperature, gravitational, and flow fields. These methods have only recently been made sufficiently powerful to meet the objectives of the proposed work, including fully three-dimensional simulations of multiple drops. The theoretical work was complemented by ground-based experiments with transparent systems, for which drop deformation, coalescence, and phase separation may be directly observed and quantified. This research was undertaken in two subtasks:

- (i) *Deformation Effects on Coalescence*—An asymptotic analysis was performed for drops or bubbles having small deformations (due to their small size and/or large interfacial tensions), based on a combination of lubrication theory and boundary-integral theory for close

approach and film drainage. This analysis is complemented by axisymmetric and three-dimensional boundary-integral numerical calculations for large deformations. Theoretical predictions of the conditions which yield coalescence, noncoalescence, or breakup were tested with microvideo experiments for interactions of deformable drops.

- (ii) *Migration and Phase Separation in Concentrated Emulsions*—The spatially-inhomogeneous population dynamics equations were solved to predict phase separation rates in the presence of a temperature gradient or gravitational field for dispersions of drops or bubbles at moderate concentrations, at which both migration and coalescence are important. For concentrated emulsions of large, deformable drops, calculation of the separation rate was made possible for the first time using three-dimensional boundary-integral/multipole simulations. The provocative hypothesis that undesirable coalescence and phase separation can be controlled by proper combination of gravitational and thermocapillary effects may be tested experimentally.

## SIGNIFICANCE

This research provides fundamental understanding of how drop or bubble migration due to residual gravity and/or thermocapillary effects interacts cooperatively with coalescence to promote macroscopic phase separation of an immiscible dispersion. The findings help resolve some critical issues, such as the roles of concentration, viscosity, interfacial tension, and other parameters on the coalescence process. The experiments and theory also provide a basis for predicting and controlling the rate of phase separation in space science applications such as processing of liquid-phase-miscibility-gap materials, gassing and degassing molten materials and cell cultures, and aqueous biphasic partitioning systems. In addition, the results are relevant to more traditional applications involving coalescence and phase separation in liquid-liquid and gas-liquid dispersions, including extraction, raindrop growth, flotation, emulsification, and creaming.

## PROGRESS

The asymptotic theory for the effects of small deformations on drop and bubble coalescence in gravitational motion was completed previously (Rother *et al.*, 1997), and it has now been extended to the interaction of two nearly spherical drops or bubbles in a temperature field (Rother and Davis, 1999). The results show that the collision efficiency (a dimensionless coalescence rate) decreases sharply with increasing drop size when deformation becomes important (Figure 1). The approach was also extended to dilute emulsions in linear flows (Rother and Davis, 2001, 2003a). The results predict that the average drop size increases due to coalescence but then levels out due to small deformations arresting the coalescence, thereby offering an alternative explanation to the commonly held theory that the average size plateaus due to a balance between coalescence and breakup. Most recently, the effects of surfactants on inhibiting drop coalescence was investigated for Brownian and/or gravitational motion of small spherical drops with nearly uniform coverage of insoluble surfactant molecules (Rother and Davis, 2003b).

A boundary-integral code described previously (Zinchenko *et al.*, 1997) has been improved with a new, curvatureless formulation (Zinchenko and Davis, 1997; Zinchenko *et al.*, 1999) and

with mesh adaptation and stabilization (Zinchenko and Davis, 1998; Zinchenko *et al.*, 1999) to study the interaction and shape evolution of deformable drops and bubbles in a gravitational field at higher Bond number (where the Bond number represents the ratio of gravitational and interfacial-tension forces on the larger drop). Bubbles and drops with low viscosity tend to become aligned and coalesce due to their shape deformations (Figure 2), as observed and described previously by Manga and Stone (1993, 1995). Systematic calculations of coalescence efficiencies (Zinchenko *et al.*, 1999) are in good agreement with experimental results for bubbles (Manga & Stone, 1995). In contrast, drops with modest viscosity become stretched and may break (Figure 3). We have also observed these phenomena in experiments with glycerol/water drops in castor oil (Figure 4).

A comprehensive set of experiments on the buoyancy interactions of two deformable drops was undertaken (Kushner *et al.*, 2001). We were able to demarcate the regions in parameter space which separate coalescence and breakup phenomena, showing good agreement with previous boundary-integral simulations. A new phenomena of ‘suckthrough’ or ‘swallowing’ was identified, where the trailing drop is sucked through the center of the leading drop and then rotates around behind it and repeats the process (Figure 5).

The boundary-integral code for two interacting drops was extended to the case of thermocapillary motion (Rother *et al.*, 2002). For this case, a new method of singularity subtraction was developed to handle the jump in tangential stress across the interfaces of the drops due to the interfacial tension gradient. As shown in Figure 6, the results for small capillary numbers are in good agreement with those for spherical drops. Larger deformations are achieved at higher capillary numbers, but these conditions are not feasible in practice because they imply a relatively large change in interfacial tension across each drop.

An axisymmetric boundary-integral code was also written and used to simulate buoyancy interaction of two drops aligned vertically. Conditions were determined for breakup of a trailing smaller drop (due to stretching and neck pinchoff), breakup of a leading larger drop (due to dimpling and plume formation), and deformation-induced capture of the smaller drop by the larger drop, as illustrated in Figure 7 (Davis, 1999). An axisymmetric code for thermocapillary migration of two unequal drops was developed previously (Zhou and Davis, 1996).

Good progress on the simulation of many deformable drops (c.f. Zinchenko and Davis, 1998, 2000, 2002, 2003) has been made by combining boundary-integral methods for neighboring drops with economical multipole techniques previously used in multiparticle conductivity (Zinchenko, 1994, 1998). These simulations indicate that deformation-induced drift and clustering occur (Figure 8). As a result, the average sedimentation or phase separation rate in an emulsion increases with time, even in the absence of coalescence (Figure 9). Simulations of concentrated emulsions in shear flow (Figure 10) show that even very small deformations allow the drops to more easily squeeze past each other, which decreases the effective viscosity (Figure 11). For dilute emulsions, a simplified model based on ellipsoidal drop shapes was developed (Wu *et al.*, 2002a,b). Transient calculations of drop shapes during stretching and relaxation are in good agreement with experiments by the group of Ron Larson at the University of Michigan. Drop deformations are shown to cause nonNewtonian rheology, even when both the drop and matrix phases are Newtonian.

A thermocapillary cell was constructed to observe coalescence and phase separation of small emulsion drops under the action of a temperature gradient. Initial studies were performed with vegetable-oil drops dispersed in various silicon fluids. However, these systems were abandoned because of their low interfacial tension and the miscibility of the two phases. Later experiments were performed with butyl-benzoate drops in water. The initial results show a gradual decline in the average drop size and concentration with time, indicating phase separation of the larger drops, and that this decline is reduced for antiparallel orientation of the gravitational and thermocapillary motion of the drops. An initial increase in the average drop size, indicative of coalescence, was not observed for this system. Additional experiments were performed in collaboration with Steve Hudson at Case Western Reserve University to observe drop growth due to coalescence in sheared polymer blends. The average drop size was observed to increase with time due to coalescence, and then level out due to the prevention of coalescence by small deformations, in good agreement with theory (Burkhart *et al.*, 2001). The resulting drop sizes are smaller at higher shear rates, due to greater deformation at higher shear (Figure 12).

## PERSONNEL

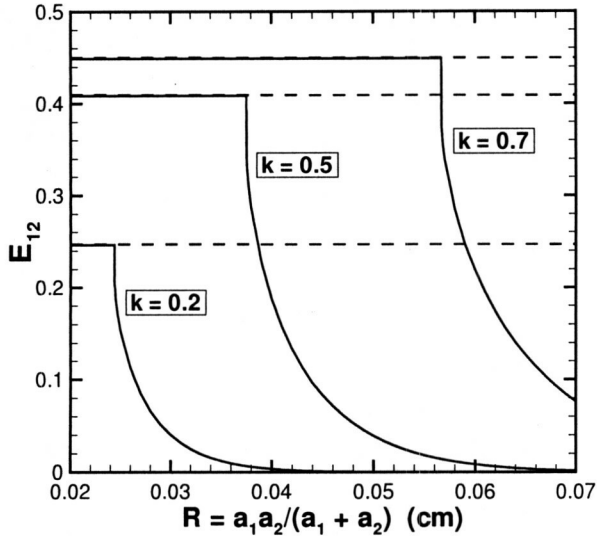
The research is primarily undertaken by Professor Robert H. Davis, Senior Research Associate Alexander Z. Zinchenko, Research Associate Michael A. Rother, and Graduate Research Assistant Yingyuan Wu. An undergraduate student, Joe Kushner, assisted with the experimental work on gravitational motion, and two undergraduate students, David Nielsen and Todd Wilder, assisted with the experiments on thermocapillary motion.

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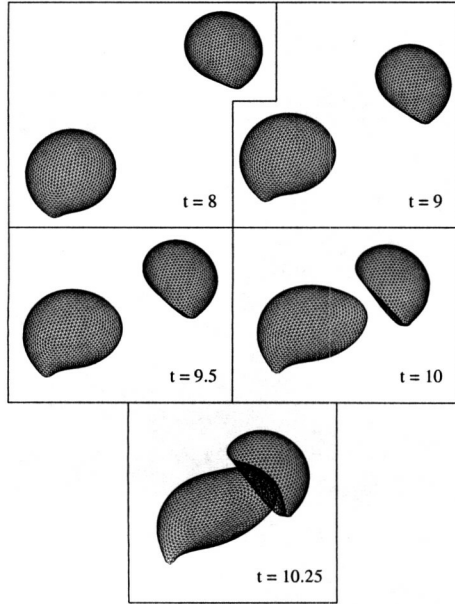
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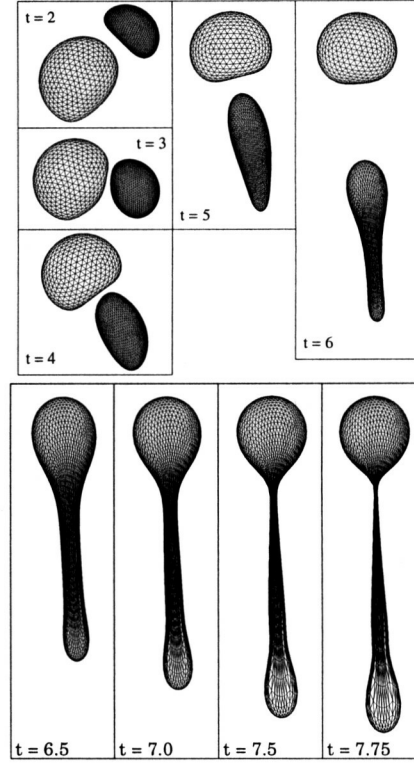
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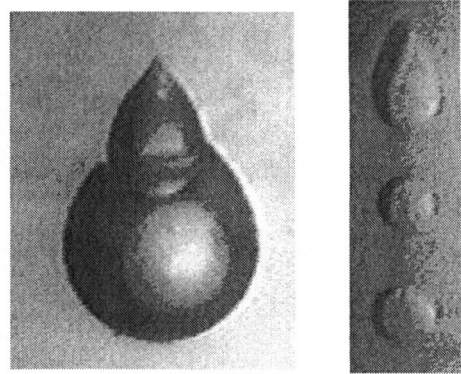
**Figure 1** – The collision efficiency of two slightly deformable ethyl salicylate drops undergoing thermocapillary motion in diethylene glycol with a temperature gradient of  $44^\circ\text{C}/\text{cm}$ . Results are shown for drop size ratios of  $k = 0.2$ ,  $0.5$ , and  $0.7$ .



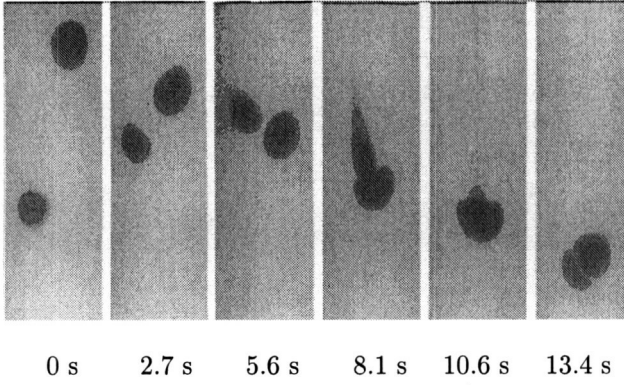
**Figure 2** – Boundary-integral simulation of the deformation-induced alignment and capture of a larger bubble by a smaller one for  $\mu = 10^3$ , size ratio  $a_2/a_1 = 0.7$ , and Bond number  $Bo = 14.3$  (from Zinchenko and Davis, 1997).



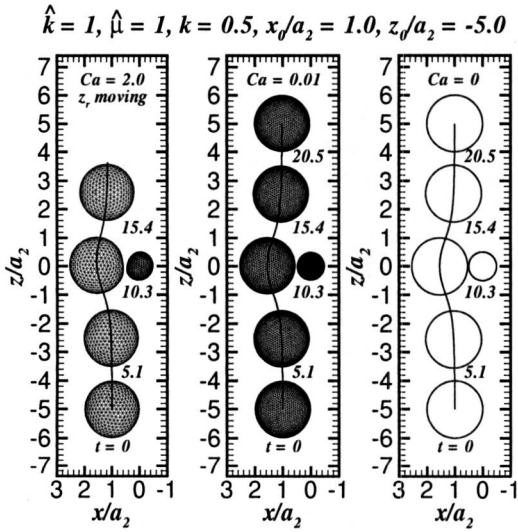
**Figure 3** – Boundary-integral simulation of the stretching and impending breaking of a smaller drop interacting with a larger one with size ratio  $a_2/a_1 = 0.7$ , drop-to-medium viscosity ratio unity, and Bond number  $Bo = 5.3$ . Only the smaller drop is shown in the final four frames.



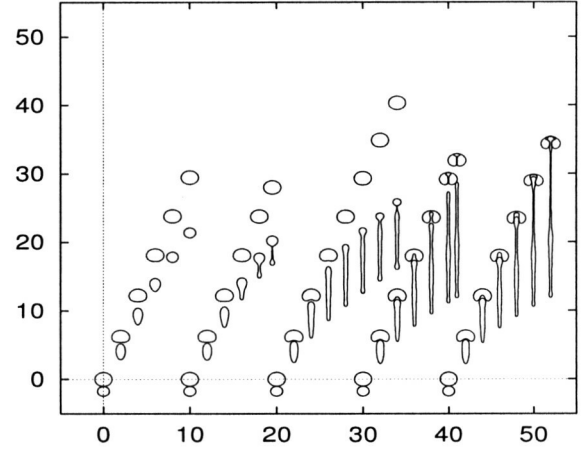
**Figure 4** – Experiments on the interaction of two rising glycerol/water drops in castor oil showing (left) capture of the smaller drop for drop-to-medium viscosity ratio  $\hat{\mu} = 0.003$  and Bond number  $Bo = 3.5$ , and (right) breakup of the smaller drop for  $\hat{\mu} = 0.4$  and  $Bo = 3.8$ .



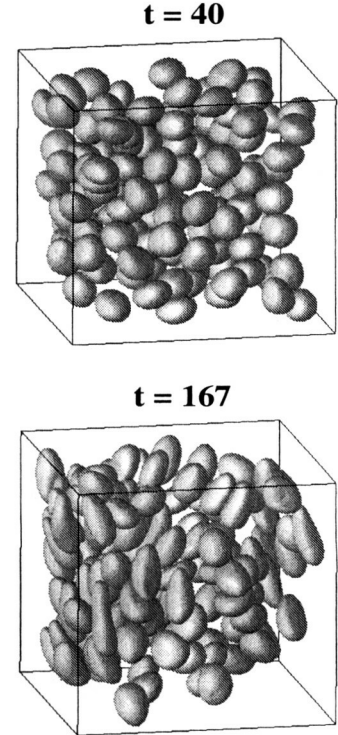
**Figure 5** – Buoyancy-driven interaction of two glycerol/water drops in castor oil. The radius ratio is  $k = 0.8$ , the drop-to-medium viscosity ratio if  $\hat{\mu} = 1$ , and the Bond number is  $Bo = 7.1$ . After the larger drop passes the smaller one, which stretches and breaks, the head of the smaller drop is swallowed by the larger drop and passes through it. This process is repeated several times (not shown).



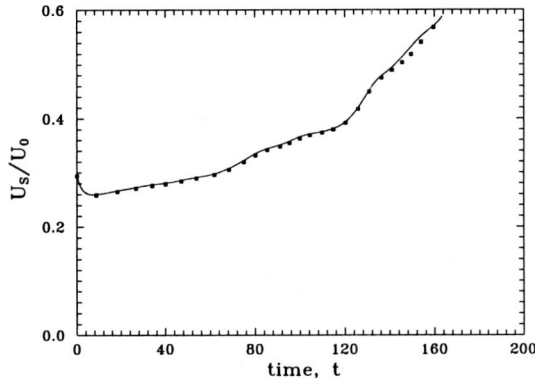
**Figure 6** – Thermocapillary motion of a large drop relative to a small drop for  $Ca = 0$  (spherical drops),  $Ca = 0.01$  (small deformations), and  $Ca = 2.0$  (large deformations), where  $Ca$  is the capillary number and represents the ratio of viscous forces to interfacial forces. The drops and suspending fluid have the same thermal conductivity and viscosity, and the size ratio is  $a_1/a_2 = 0.5$ .



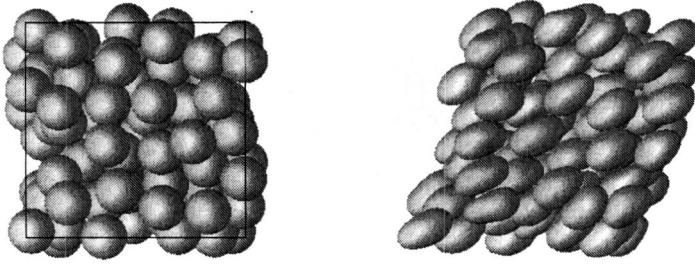
**Figure 7** – Shape evolution of two drops rising due to gravity with size ratio  $a_2/a_1 = 0.7$ , drop-to-medium viscosity ratio  $\hat{\mu} = 1$ , initial separation  $h_0/a_1 = 0.02$ , and Bond number  $Bo = 4.0, 4.5, 75., 9.5$  and  $10.5$  (left to right); the horizontal positions are shifted right by two length units for every 20 time units.



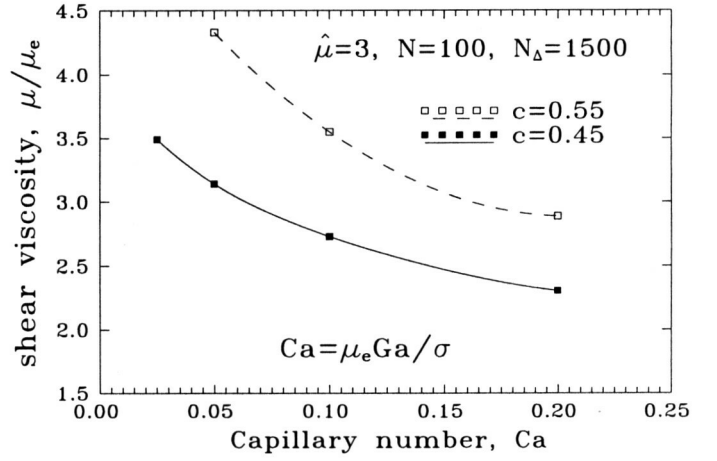
**Figure 8** – Boundary-integral simulation of gravity sedimentation of a monodisperse emulsion with  $N = 125$  drops in a cubic cell continued triple-periodically into the whole space at drop-to-medium viscosity ratio  $\hat{\mu} = 1$ , Bond number  $Bo = 1.75$ , and drop volume fraction  $c = 0.25$ .



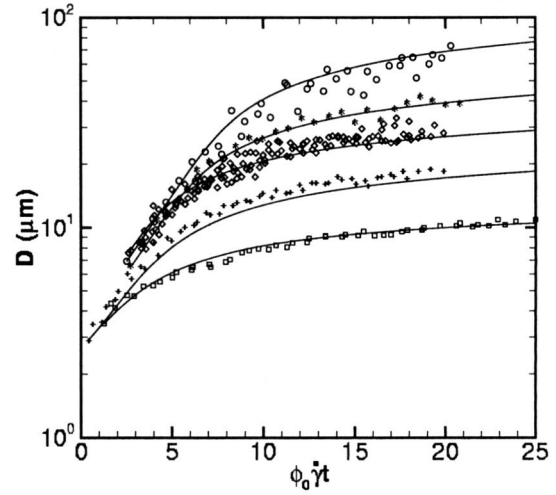
**Figure 9** – Volume-averaged sedimentation rate (divided by that of a single spherical drop) versus time for a monodisperse emulsion with drop-to-medium viscosity ratio  $\hat{\mu} = 1$ , Bond number  $Bo = 1.75$ , drop volume fraction  $c = 0.25$ , and number of drops in the periodic



**Figure 10** – Simulation of shear flow of a concentrated emulsion with drop volume fraction  $c = 0.5$ , drop-to-medium viscosity ratio  $\hat{\mu} = 4$ , and capillary number  $Ca = 0.1$ , using  $N = 100$  drops in a triply periodic cell. The initial configuration is shown on the left, and a configuration typical of steady state is shown on the right.



**Figure 11** – Effective viscosity of a sheared emulsion versus capillary number for drop volume fractions  $c = 0.45$  and  $0.55$  and for a drop-to-medium viscosity ratio of  $\hat{\mu} = 3$ , using  $N = 100$  drops in a triply periodic cell and  $N_{\Delta} = 1500$  triangles per drop.



**Figure 12** – Growth of the volume-averaged drop diameter for poly(propyleneglycol) drops in poly(ethylene glycol) subject to shear rates of 2, 5, 10, 20 and  $50 \text{ s}^{-1}$  from top to bottom. The symbols are experimental data, and the curves are theory.